

PATENT SPECIFICATION

(11)

1 573 008

ORIGINAL
CLASSIFICATION

- (21) Application No. 51904/76 (22) Filed 13 Dec. 1976 (19)
 (31) Convention Application Nos. 642560 (32) Filed 19 Dec. 1975
 642540 19 Dec. 1975
 745858 29 Nov. 1976
 745857 29 Nov. 1976 in
 (33) United States of America (US)
 (44) Complete Specification Published 13 Aug. 1980
 (51) INT. CL. ³ B32B 33/00 27/06
 (52) Index at Acceptance
 B2E 1732 407T 407U 409T 409U 413T
 413U 436S 436T 436U 448T 448U
 450T 450U 489U M



(54) METALLIZED FLEXIBLE PLASTICS AUTOMOBILE TRIM COMPONENT

- (71) We, McCORD CORPORATION, of 2850 West Grand Boulevard, Detroit, Michigan 48202, United States of America, a corporation organised and existing under the laws of the State of Michigan, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in the following statement:-
- The present invention relates to a metallised plastics article having a composite coating which is built up in a specific manner from certain selected films or ingredients.
- Vacuum metallizing of plastics surfaces has been practiced for some time. For example, see U. S. Patents Nos. 3,201,271; 3,740,254; 2,993,806; and 3,783,012. More recently, attempts have been made to manufacture automobile exterior trim components such as bumpers, bumper sections or fender extensions of a tough but flexible, abuse-resistant plastics material having a bright metal-like surface. Generally speaking, such metallized surfaces have not had the low-temperature flexibility, the resistance against impact from gravel, the corrosion resistance, and the chrome-plated appearance, required for automotive use. An article in the December 1974 issue of Modern Plastics, "Restoring the Lustre to Metallized Markets", pp. 42-46, by C. Otis Post presents a good summary. In that article it is noted with regard to making metallized coatings environmentally acceptable that: "The relationships among a plastics substrate, base coat, metallized coating, and top coat are so intricate that changing any one member usually means reformulating one or more of the others."
- According to one aspect of the invention there is provided a metallized plastics article comprising:
- a flexible elastomeric plastics substrate, the surface of which tends to degrade upon exposure to light, a light-blocking continuous pigmented polymeric layer thereon, the pigment content and thickness thereof being sufficient to ensure that any amount of light detrimental to said plastics-substrate does not pass therethrough,
 - a deposited metal film overlying the polymeric layer less than 1000 Å thick, and
 - a continuous non-opaque protective polymeric top coat over said metal film.
- According to another aspect of the invention there is provided a metallized plastics article comprising:
- a) a flexible elastomeric plastics substrate
 - b) a light-blocking pigmented primer coat on a surface of said substrate,
 - c) a base coat over said primer coat of a baked thermosetting resin,
 - d) a vacuum deposited layer thereon of a metal selected from the group consisting of chromium, stainless steel and aluminum, said layer being in the range of 200 to 1000 Å thick, and
 - e) a moisture impervious flexible film thereover of a non-opaque acrylic lacquer.
- According to a further aspect of the invention there is provided a metallized plastics article which includes a synthetic polymeric substrate that tends to degrade upon exposure to sunlight, a light blocking pigmented polymeric layer thereon, a deposited metal film overlying the polymeric layer and a transparent protective polymeric topcoat over said metal film, said metal film being minutely fissured permitting passage of light, and the pigment content and thickness of said pigmented polymeric layer being sufficient to stop passage of said sunlight from said fissures.
- And according to a further aspect of the invention there is provided a metallised plastics

article comprising

- (a) a flexible elastomeric plastics substrate,
- (b) a pigmented primer coat on a surface of said substrate,
- (c) a clear base coat over said primer coat of a baked blend of an aliphatic urethane resin
- 5 with an anhydride cured epoxy resin,
- (d) a vacuum deposited layer thereon of a metal, and
- (e) a clear abuse resistant film thereover of a baked blend of acrylic, aliphatic urethane and melamine resins.

The metallizing may involve the use of vacuum deposited chromium or stainless steel such as a "ferrous-chrome" containing 13% to 30% chromium when the part is designed for exterior use on an automobile. Such a stainless steel or chromium coated part can also be used in the interior of an automobile such as for trim for an instrument cluster. One may prefer to use aluminum instead of stainless steel where weathering and abuse resistance are not too important as aluminum gives a more pleasing chromium plated-like appearance, i.e. it more nearly duplicates the appearance of conventional electroplated chrome parts. However, when a thin layer of aluminum oxidizes it becomes transparent or translucent and the metallic luster is lost. In an exterior application such as a bumper section, if there is a break or blemish caused by a stone nick or the like, an aluminum layer disappears at the break or blemish point in a short period of time and then will continue to oxidize and disappear until the entire aluminum layer is gone.

The base plastics material from which the part is made is a tough but flexible elastomer, preferably an injection molding grade thermoplastic polyurethane (TPU). By "flexible elastomer" is meant a natural or synthetic thermoplastic or thermoset plastics material or polymer having an extensibility of greater than approximately 30 percent, as compared to a "rigid" plastics material which may be considered to have an extensibility of less than 10 percent. While it is preferred to use a molded thermoplastic urethane because of its other properties, such a urethane is more deleteriously affected by sunlight than many other plastics, that is, it is light sensitive.

An article of the desired shape made from the elastomer, after surface cleaning if required, may be successively coated in accordance with the present invention with preferably four well-bonded layers or films to produce the final lustrous metallic appearance desired.

The cleaned plastics part is first prime coated with a pigmented and thus light-blocking urethane lacquer having a dry film thickness of 0.8 to 1.2 mils, which is air flashed and baked. While aromatic urethanes have been used, the urethane is preferably an aliphatic one which is inherently more light stable. This is followed by a base coat of a melamine formaldehyde resin or preferably, a urethane-epoxy resin having a dry film thickness of about 0.8 to 1.2 mils. The base coat is also baked, and if it were applied directly to the plastic substrate, it would not adhere well. On the other hand, the pigmented urethane lacquer prime coat will not flow readily and form the level, sheeny and smooth uniform surface required for the vacuum deposited metal. Desirably, the base coat should also be light stable.

Depending on the appearance desired in the final part, the base coat can be applied to be sheeny or to be matte appearing. It is preferred to apply the base coat "wet-on-wet" directly onto the air-flashed but not completely baked primer as better intercoat adhesion is obtained. The base coat when dry may be glossy so that the finished article has a sheeny metallic appearance.

The metal is then vacuum deposited onto the base coat using preferably the resistance method. Electron beam and sputtering vacuum depositing can also be used. Sputtering gives a deposit that is brighter appearing than the others, but a lacquer top coating thereover tends to microcrack in the metal layer. Resistance coating is favored as the required investment in equipment is substantially less.

The metal coating is preferably 200-1000 Å thick -- thick enough to develop the proper metallic color. If stainless steel is used, its chromium content is essential, but the steel can also have incorporated therein minor amounts of nickel and/or magnesium and/or other metals. The use of essentially pure chromium is included within the ambit of this invention because, contrary to what some believed, it was found that chromium could be successfully vacuum deposited for this application. Essentially pure aluminum gives the more pleasing appearance and most closely matches that of traditional electrodeposited chromium on metal parts. Chromium deposited by resistance vacuum metallizing is the next most effective in matching electrodeposited chromium.

The thin metal coating is not, of course, resistant to mechanical abuse and to long term weathering and needs to be protected. While various flexible abuse-resistant non-opaque top coats, such as an acrylic lacquer might be used, it has been found that a clear lacquer derived from a blend of acrylic, aliphatic urethane and melamine resin has definite advantages and is to be preferred. This particular top coat can also be used in other applications such as for the protection of painted parts.

The film thickness of the top coat is preferably in the range of 1.3 to 1.6 mils, dry basis, and it is preferably thoroughly baked, e.g. at 250°F, but too high a temperature may cause some yellowing and/or iridescence. The top coat is formulated to adhere to the metal layer as well as to the base plastics material. By deliberately overlapping the top coat, the metal coat and the two underlying layers can be "encapsulated" between it and the base plastics material eliminating edge delamination.

The development work on this invention turned up an interesting finding, viz: that light may penetrate the metal coating and base coat film and reach the surface of the underlying primer coat, causing degradation thereof and interfacial loss of adhesion between the base coat and the primer coat. That light penetrates the metal film, which appears to the eye to be continuous and opaque, is surprising. This was found to be so as follows: When a metallized layer deposited on a film of the base coat supported on a glass plate is exposed to visible light, including ultraviolet light rays, the light will not pass through. When, however, the acrylic top coat is applied thereover and baked, some of the light will pass through. It is believed that this is because minute, microscopic cracks or fissures through the metal film were formed which allowed the light to pass. Apparently the solvents normally used in the top coat material and the difference in thermal expansion of the metal and resin films during baking cause these minute cracks to appear.

As the light does pass through the metal layer, as the base coat is not pigmented, and as the thermoplastic urethane base part is quite light sensitive, the skilled in the art will appreciate that it is quite desirable to make the primer coat light opaque and to use a resin therein that is, preferably, inherently light stable, such as an aliphatic urethane. Long term outdoor, e.g. Florida sunshine for one year, weathering tests have conclusively established that interfacial adhesion loss will occur between the base coat and the primer coat before it will occur at the interfaces of the other layers. Use of a properly formulated, pigmented and applied primer coat will offset this interfacial adhesion loss.

There is little question that this finding of light penetration and effect is an important one that lends considerable merit to the present claim for inventiveness for the described multi-layered metallized product. And, of course, as the metal film is in a sense deliberately micro-cracked or minutely cracked in a controlled regulated manner, this permits later flexing and bending of the product without appreciable or too objectionable change in its appearance. Moreover, light is reflected back through these microscopic cracks to some extent, and this characteristic can be used to esthetic advantage. A white or tinted light-blocking pigmented primer coat can be effectively employed to advantageously change the appearance of the metal layer and enhance the overall appearance of the multi-layered metallized plastics article.

THE DRAWING

The drawing is a greatly enlarged schematic cross-sectional view of a metallized surface made according to this invention, in which the number designating the layers are:

- 1) Injection molded thermoplastic urethane.
- 2) Baked urethane lacquer.
- 3) Baked melamine formaldehyde resin.
- 4) 800 Å vacuum deposited ferrous-chrome-20 stainless steel.
- 5) Clear acrylic lacquer.

EXAMPLE I

The sample part made was a 1975 Cadillac (Registered Trade Mark) Fender Extension, part number X1605647.

An elastomeric thermoplastic urethane was "in house" manufactured from a grafted poly (oxypropylene) diol (Union Carbide Company's NIAx D-432, (Niax is a Registered Trade Mark) 270 Park Avenue, New York, New York 10017), 100 parts by weight; polytetramethylene ether glycol (Quaker Oats Company Polymeg 100, Merchandise Mark Plaza, Chicago, Illinois 60654), 28 parts; 4', 4' diphenylmethane diisocyanate, 86 parts; and 1, 4 butanediol, 26 parts. This thermoplastic urethane is fully described in U.S. Patent No. 3,933,938. Commercially available Uniroyal thermoplastic urethane designated E-2A could also be used (Uniroyal, Inc., 1230 Avenue of the Americas, New York, New York 10020). The nature of the flexible urethane substrate does not appreciably affect the performance of the applied coating. The urethane cannot be so stiff or rigid that it will not serve its intended function as a flexible trim component nor can it be too flexible or elastomeric. The present coating system can, of course, be applied and used with a substantially more rigid substrate, but other methods of bright trimming such as plating may be more economical to use on firm or hard surfaces.

The urethane lacquer primer was a standard production item supplied by PPG Industries, 3800 West 143rd Street, Cleveland, Ohio, under the code designation DEL-600-32906. Any

equivalent light-blocking primer that adheres well to the molded thermoplastic urethane can be used. The one used was a thermoplastic and was not considered too stable to ultraviolet light as it was an aromatic urethane. It was pigmented to a gray color with black and white pigments. The primer was sprayed as supplied by the manufacturer in three or four passes onto the properly cleaned surface at room temperature to a thickness of 1.0 ± 0.2 mils (dry basis).

The applied coating requires an air flash for 10 minutes or so, but it was not baked at this point. One of the findings made during the development of this invention was that the subsequent base coat could be applied "wet-on-wet" with improved intercoat adhesion and the consequent saving coming from the elimination of the primer baking step.

The base coat applied over the primer also was a commercially available tough melamine formaldehyde resin, diluted to spray viscosity of 38 ± 2 seconds (No. 1 Zahn Cup). The base coat was SM-1240-6, supplied by Red Spot Paint & Varnish Co., Inc., 100 Main Street, Evansville, Indiana. It was applied to a thickness of 1.0 ± 0.2 mils. The coating was air flashed for 15 minutes, and then the two coatings were baked for 45 minutes at $250^\circ\text{F} \pm 5^\circ\text{F}$ (oven air temperature).

After cooling to room temperature, the parts were vacuum metallized using an Airco Temescal (Registered Trade Mark) electron beam metallizer. The metal used was a ferrous-chrome-20 stainless steel supplied by Airco Temescal, 2850 Seventh Street, Berkeley, California 94710, and it was applied to a thickness of $800 \text{ \AA} \pm 200 \text{ \AA}$. The procedure used was as follows:

- 1) Metallizer was brought up to and maintained at steady state condition as per manufacturer's instructions.
- 2) Samples were loaded into the interlock chamber.
- 3) Chamber was sealed and brought down to proper vacuum.
- 4) Samples were moved into the metallizing chamber, through the metal vapor cloud and back to the interlock chamber.
- 5) Interlock chamber was pressurized and the samples were removed.

The top coat was a solvent based acrylic lacquer spray applied by conventional methods. The base material is supplied by Pan Chemical Corp., 1 Washington Avenue, Hawthorne, New Jersey, as 68-189A or 68-202A. The coating was applied to a thickness of 1.3 to 1.6 mils (dry basis) followed by air flashing for 15 minutes and baking at $150^\circ\text{F} \pm 2^\circ\text{F}$ (oven air temperature) for 60 minutes.

Thermoplastic urethane (TPU) Cadillac Fender Extensions made with the "in house" material and metallized and coated as above described were subjected to various tests with the results as given in the following Table.

TEST RESULTS

Test	Results
200 Weatherometer Hours (3)	Slight dulling and water spotting
Water Immersion (3)	Pass
Tape Adhesion (3)	Pass
Thermal Cycle	Pass
C.A.S.S. Test (1)	Pass
Cold Flex (3) Substrate	Pass
Finish	Cracked
Gravelometer (SAE Test J-400)	Pass
Salt Spray (2)	Pass
Gravelometer plus C.A.S.S. (3)	Pass
Gravelometer plus Salt Spray (3)	Pass
Car Wash (3) at 1/2%	Pass
at 5%	Pass
(1) General Motors Test 4476-P	
(2) General Motors Test 4298-P	
(3) According to Cadillac Bright Trim Specifications	

EXAMPLE II

The coating of Example I is applied to an instrument gauge rim with the only difference being that an aluminum is used in place of the stainless steel. The aluminum is a 99.99% high purity aluminum supplied by R. H. Cheney Inc. of Attleboro, Massachusetts 02703, and is applied to a thickness of $800 \text{ \AA} \pm 200 \text{ \AA}$. This part is suitable for use in the interior of an automobile.

For critical exterior use, PPG Industries Durethane 300 is preferably used as the primer. This is a pigmented enamel instead of a lacquer and is based on a thermosetting resin. The resin is an aliphatic urethane which is more light stable than the aromatic urethane of the DEL-600-32906. Durethane 300 is weatherable, flexible at low temperatures and possesses good adhesion affinity for the molded thermoplastic urethane surface.

Durethane 300 is white in color and it has been found that this underlying white coat material enhances the pleasing metallic appearance of the product, i.e. the metal film is usually thin enough such that the color of the primer coat can be seen through the metal film. Obviously, in some instances it may be desirable to tint the primer coat to improve the appearance of the part. Also, the use of a white primer coat has the additional advantage that if the metal film is scratched or scored, the white shows through, i.e. one sees the white which is complimentary to the metal and not some disfiguring color such as black or gray.

The following formulation has been found to work exceptionally well as a base coat formulation in place of the previously described Red Coat SM-1240-6.

		<i>Parts by weight</i>	
	Aliphatic urethane #1 (40% solids)	50.0	
	Epoxy resin (1)	3.0	
20	HHPA (2)	3.0	20
	Catalyst solution (3)	4.0	
	Cellosolve acetate (4)	46.0	
	Methyl-ethyl ketone	<u>50.0</u>	
25		156.0	25

(1) 3, 4 epoxy cyclohexylmethyl -3,4 epoxy cyclohexane carboxylate

(2) hexahydrophthalic anhydride

(3) five parts by weight uranyl nitrate, balance Cellosolve acetate

(4) Union Carbide trade name for 2, ethyloxyethyl acetate.

Cellosolve is a Registered Trade Mark.

The aliphatic urethane solution #1 was based on reacting epsilon caprolactone polyester diols and triols with cyclohexyl diisocyanate (CHDI) at 50% solids in toluene, followed by dilution to the 40% solids level with additional toluene. The polyesters were Union Carbide Corporation's NIAx PCP-0200 (the diol) and NIAx PCP-0300 (the triol) and were reacted as follows:

		<i>Parts by weight</i>	
40	PCP-0300	14.698	40
	PCP-0200	3.498	
	CHDI (1)	21.799	
	Toluene	59.994	
45	Catalyst (2)	<u>0.011</u>	45
		100.000	

(1) Hylene W--E.I. duPont de Nemours & Co., 1007 Market Street, Wilmington, Delaware 19808.

(2) Dibutyl tin dilurate

Hylene is a Registered Trade Mark.

As can be seen, this base coat formulation is composed of an aliphatic amine blended with an anhydride cured epoxy, with the curing being catalyzed by the uranyl nitrate. This blend was formulated to optimize flexibility versus hardness and to provide the excellent metal adhesion that the epoxies are noted for. eight ratio of urethane resin to cured epoxy resin in the above is preferably about 3 to 1 but this can vary from 1 to 1 to 1 to 2.

The following formulation has been found to work better as a top coat formulation than the previously described Pan Chemical's 68-202A:

	<i>Parts by weight</i>	
	Aliphatic urethane #2 (40% solids)	30.0
	Acrylic (1)	16.0
5	Melamine (2)	3.0
	Catalyst (3)	0.3
	Methyl-ethyl ketone	50.0
	Cellosolve acetate (4)	60.0
	Toluene	40.0
10		199.3

- (1) Cyanamid XC-4011 (Carboxyl functional acrylic)--American Cyanamid Co., South Cherry Street, Wallingford, Connecticut 06492 15
- (2) Cyanamid 303 (hexamethoxymethyl melamine)
- (3) Cyanamid 4040 (acid catalyst)
- (4) Union Carbide trade name for 2, ethyloxyethyl acetate.
- The aliphatic urethane solution #2 was based on reacting epsilon caprolactone polyester triol (NIAAX PCP-0300) and 1, 6 hexane adipate diol with cyclohexyl diisocyanate (CHDI) at 40% solids level as follows: 20

	<i>Parts by weight</i>	
25	CHDI (1)	20.092
	Catalyst (2)	0.011
	PCP-0300	13.495
	1, 6 Hexane adipate diol (3)	6.407
	Toluene	59.995
30		100.000

- (1) Hylene W
- (2) Dibutyl tin dilaurate
- (3) Ageflex 6-1000-Witco Chemical Co., 277 Park Avenue, New York, New York 10017 35
- The weight ratios of the resins in this top coat are such that the aliphatic urethane and acrylic resins are used in about equal amounts, although up to 5 times as much urethane as acrylic can be used. The melamine will usually amount to 5 to 20 weight percent of the acrylic resins.
- TPU Cadillac fender extensions made with this metallized bright trim system give the following test results: 40

TEST RESULTS

	<i>Test</i>	<i>Results</i>	
45	500 Weatherometer Hours (3)	Slight dulling and water spotting	45
	Water Immersion	Pass	
	Tape Adhesion (3)	Pass	
	Thermal Cycle	Pass	
	C.A.S.S. Test (1)	Pass	
50	Cold Flex (3) Substrate	Pass	50
	Finish	Pass	
	Gravelometer (SAE Test J-400)	Pass	
	Salt Spray (2)	Pass	
	Gravelometer plus C.A.S.S. (3)	Pass	
55	Gravelometer plus Salt Spray (3)	Pass	55
	Car Wash (3) at 1/2%	Pass	
	at 5%	Pass	

- (1) General Motors Test 4476-P
- (2) General Motors Test 4298-P 60
- (3) According to Cadillac Bright Trim Specifications
- WHAT WE CLAIM IS:-**
1. A metallized plastics article comprising:
- a flexible elastomeric plastics substrate, the surface of which tends to degrade upon exposure to light, a light-blocking continuous pigmented polymeric layer thereon, the pigment 65

content and thickness thereof being sufficient to ensure that any amount of light detrimental to said plastics substrate does not pass therethrough,

deposited metal film overlying the polymeric layer less than 1000 Å thick, and a continuous non-opaque protective polymeric top coat over said metal film.

5 2. The article of claim 1 wherein said pigment is light coloured. 5

3. The article of claim 1 wherein said continuous pigmented polymeric layer is immediately contiguous to said plastics substrate as a primer coat and has had applied directly thereto a base coat of a stable thermosetting resin on to which has been directly applied said metal film by vacuum deposition.

10 4. The article of claim 3 in which said article is an exterior automobile trim component, said metal film is formed from a metal selected from the group consisting of stainless steel and chromium, said primer coat is a pigmented urethane lacquer having a dry film thickness of 0.8 to 1.2 mils, said base coat is baked melamine formaldehyde resin having a dry film thickness of 0.8 to 1.2 mils, and said top coat is a baked acrylic lacquer having a dry film thickness of 1.3 to 1.6 mils. 10 15

5. The article of claim 3 when said article is an interior automobile trim component, said metal film is of aluminum, said primer coat is a pigmented urethane lacquer having a dry film thickness of 0.8 to 1.2 mils, said base coat is a baked melamine formaldehyde resin having a dry film thickness of 0.8 to 1.2 mils, and said top coat is baked acrylic lacquer having a dry film thickness of 1.3 to 1.6 mils. 15 20

6. A metallized plastics article comprising:

a) a flexible elastomeric plastics substrate, 20
b) a light-blocking pigmented primer coat on a surface of said substrate,
c) a base coat over said primer coat of a baked thermosetting resin,
25 d) a vacuum deposited layer thereon of a metal selected from the group consisting of chromium, stainless steel and aluminum, said layer being in the range of 200 to 1000 Å thick, and

e) a moisture impervious flexible film thereover of a non-opaque acrylic lacquer.

7. The metallized plastics article of claim 6 wherein said primer coat and said base coat have the characteristics of having been spray-applied wet-on-wet and baked together and wherein said flexible film of said acrylic lacquer extends over the edges of said vacuum deposited layer, base coat, and primer coat onto said substrate, thereby encapsulating the three intermediate coats. 30

8. The metallized plastic article of claim 7 when an automobile trim component and wherein said plastics substrate is a molded thermoplastic urethane. 35

9. The automobile trim component of claim 8 wherein said base coat, when dry, is glossy such that the finished article has a sheeny metallic appearance.

10. A metallized plastics article which includes a synthetic polymeric substrate that tends to degrade upon exposure to sunlight, a light-blocking pigmented polymeric layer therein, a deposited metal film overlying the polymeric layer and a transparent protective polymeric topcoat over said metal film, said metal film being minutely fissured permitting passage of light, and the pigment content and thickness of said pigmented polymeric layer being sufficient to stop passage of said sunlight from said fissures. 40

11. The article of claim 10 wherein said pigment content imparts a light color to said polymeric layer and said metal film is thin enough to permit the presence of said light color to be visually apparent, as compared with the absence thereof. 45

12. The article of claim 10, in which said topcoat comprises a blend of acrylic, aliphatic urethane and melamine resins which have been laid down as a lacquer and then dried and baked.

13. The article of claim 12 when an automobile exterior trim component and wherein in said blend the weight ratio of said aliphatic urethane resin to said acrylic resin is in the range of 1/1 to 5/1 and said melamine resin is in the range of 5% to 20% by weight of acrylic resin. 50

14. A metallized plastics article comprising (a) a flexible elastomeric plastics substrate, (b) a pigmented primer coat on a surface of said substrate, 55 (c) a clear base coat over said primer coat of a baked blend of an aliphatic urethane resin with an anhydride cured epoxy resin, (d) a vacuum deposited layer thereon of a metal, and (e) a clear abuse resistant film thereover of a baked blend of acrylic, aliphatic urethane and melamine resins. 60

15. The article of claim 14 in which the vacuum deposited layer is a metal selected from the group consisting of chromium, stainless steel and aluminum and has a thickness of 200 Å to 100 Å. 60

16. A metallized plastics article substantially as herein described or illustrated in the accompanying drawings.

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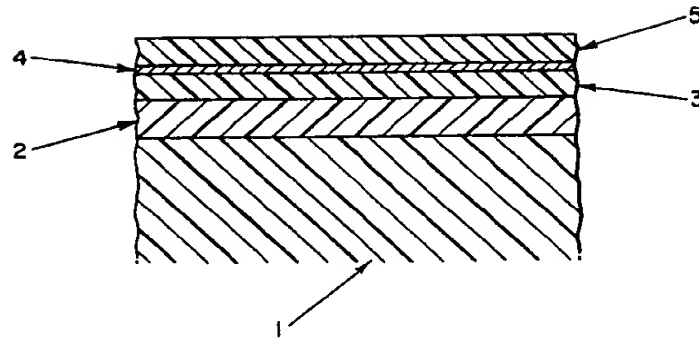
Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*



1. INJECTION MOLDED THERMOPLASTIC URETHANE
2. BAKED URETHANE LACQUER
3. BAKED MELAMINE-FORMALDEHYDE RESIN
4. 800 Å VACUUM DEPOSITED FERROUS-CHROME 20
STAINLESS STEEL
5. CLEAR ACRYLIC LACQUER

